



Electrochemical and photophysical characterization of non-peripherally-octaalkyl substituted dichlorotin(IV) phthalocyanine and tetrabenzotriazaporphyrin compounds

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ABSTRACT: Three non-peripherally substituted tin(IV) macrocyclic compounds, octahexylphthalocyaninato dichlorotin(IV) (**3a**), octahexyltetrabenzo-5,10,15-triazaporphyrinato dichlorotin(IV) (**3b**) and octadecylphthalocyaninato dichlorotin(IV) (**3c**) were synthesized and their photophysical and electrochemical behavior studied. Complex **3b**, containing a CH group in place of one of the aza nitrogen atoms of the phthalocyanine core, shows a split Q-band due to its lower symmetry. The triplet state quantum yields were found to be lower than would be expected on the basis of the heavy atom effect of tin as the central metal for phthalocyanine derivatives (**3a** and **3c**). In contrast, **3b** shows a triplet quantum yield $\Phi_T = 0.78$. The triplet state lifetimes were solvent dependent, and were higher in tetrahydrofuran than in toluene. Cyclic voltammetry and spectroelectrochemistry of the complexes revealed only ring-based redox processes. Copyright © 2007 Society of Porphyrins & Phthalocyanines.

KEYWORDS: tin phthalocyanine, tin tetrabenzotriazaporphyrin, cyclic voltammetry, spectroelectrochemistry, triplet quantum yields, triplet lifetimes, fluorescence quantum yields.

INTRODUCTION

Phthalocyanines (Pcs) are 18π electron macrocycles that have been the subject of continuous investigation for over 7 decades. Much of this research effort has been inspired by their wide range of properties, and many metallated derivatives (MPcs) have found applications, or show potential for exploitation, in a variety of fields. Long established as commercial dyes and pigments and industrial catalysts [1], Pcs are now also utilized in electrophotography, data storage systems, the security printing industry [2], and as photosensitizers for photodynamic therapy [3, 4]. They also have con-

siderable potential for use in chemical sensing [5] and non-linear optical devices [6-8]. Unsubstituted Pcs have limited solubility in many solvents but a number of the applications referred to are dependent upon solubilizing materials in particular solvents. To increase solubility, substituents can be introduced at the peripheral or non-peripheral positions of the ring. Tetra-substituted Pcs are usually more soluble than the corresponding octa-substituted phthalocyanines due to the formation of constitutional isomers and the dipole moment that results from the unsymmetrical arrangement of the substituents [9-11]. Appropriately substituted octa-substituted Pcs on the other hand can be obtained isomerically pure. Substitution at the more sterically crowded α (non-peripheral) positions with, for example, alkyl groups, reduces aggregation tendencies and enhances solubility in non-polar solvents more so than substitution at β (peripheral)

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